CHAPTER 28

CHEMICAL EFFECT OF A CURRENT

All discussion on current so far, has assumed that current is a movement of electrons only. Electrons in a solid such as copper or aluminium are termed free electrons, because they move at random throughout the metal, ionising the metal atoms in the process. When an e.m.f. is applied to the ends of a metal conductor, the electrons in the conductor move to the positive terminal of the e.m.f., due to the electrostatic laws. Why then don't the positive ions in the metal conductor move towards the negative side of the source. The answer is that the positive ions in a metal are locked into the metallic structure and cannot be shifted. In other materials and solutions, however, this is not always so. Some of the occasions where both electrons and ions do contribute to current flow are studied in this Chapter.

28.1 IONISATION

Certain compounds will break up or 'dissociate' when immersed in a fluid. The compounds may by crystal or liquid form. When the compounds dissociate they form positive and negative ions. Some of the compounds in this category are listed in Table 28.1.

Table 28.1

NAME	CHEMICAL FORMULA	+ ION	- ION
Sulphuric Acid	$H_2\ SO_4$	$2\ H^+$	$SO_4^=$
Sodium Chloride (Salt)	Na CL	Na^+	CL^-
Copper Sulphate	$Cu\ SO_4$	Cu^{++}	$SO_4^=$
Silver Nitrate	$Ag\ NO_3$	Ag^+	NO_3^-

When these compounds dissociate in water they have the ability to conduct electric current through the solution. They are called electrolytes.

28.2 THE ELECTROLYTIC CELL

When two electrodes are immersed in an electrolyte and current is supplied from an e.m.f. source an electrolytic cell is formed. The electrodes may be of different or identical materials (note the difference from the chemical cell). The electrolytic cell is formed with the direct intention of producing chemical reactions within the cell. The electrolyte in solution dissociates into positive and negative ions. (Figure 28.1).

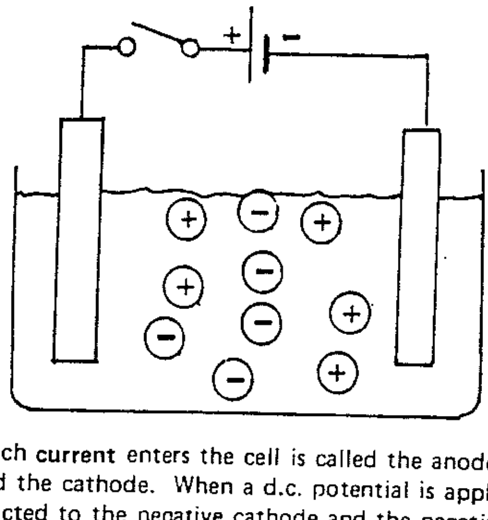

Figure 28.1

The electrode by which current enters the cell is called the anode, while the electrode by which current leaves the cell is called the cathode. When a d.c. potential is applied to the cell, the positive ions in the electrolyte will be attracted to the negative cathode and the negative ions will be attracted to the positive anode. (Figure 28.2)

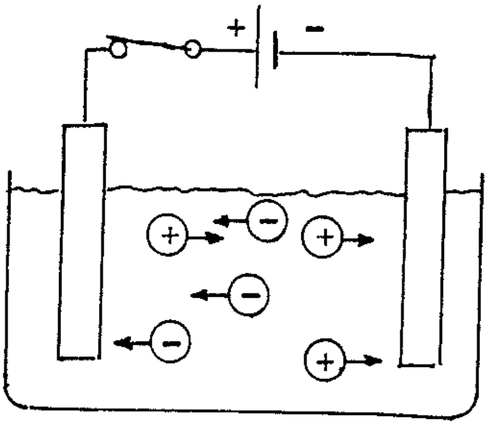

Figure 28.2

The chemical reactions within the cell are determined by the materials used as electrodes. These materials may be active or inert. In the active electrode cell, chemical reactions occurring at the electrodes cause the anode to pass into solution and be deposited on the cathode. In the inert cell, the state of the electrodes remains unaltered.

28.3 ELECTROLYTIC CELL WITH ACTIVE ELECTRODES

A simple electrolytic cell consisting of copper electrodes and a solution of copper sulphate is shown in Figure 28.3.

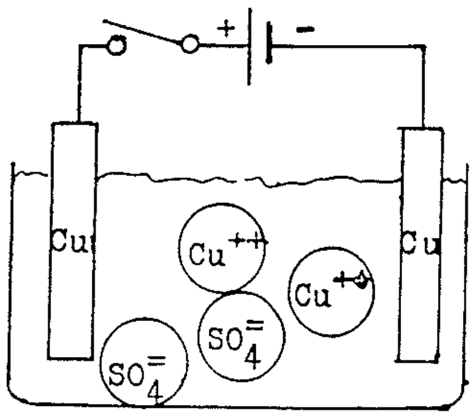

Figure 28.3

The electrolyte consists of positive copper ions (Cu^{++}) and negative sulphate ions ($SO_4^=$). The negative sulphate ions are attracted to the positive anode where they combine with copper ions from the anode to form copper sulphate again. For this combination to occur the copper atom in the anode must release two electrons. The positive copper ions migrate to the negative cathode where it accepts two electrons and becomes a copper atom. (Figure 28.4).

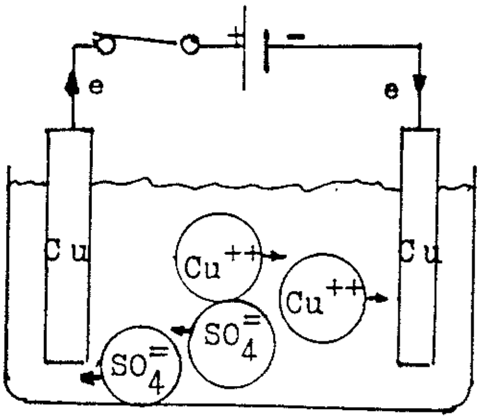

Figure 28.4

The copper sulphate formed at the anode dissociates in solution and becomes copper and sulphate ions again. The copper atoms formed at the cathode adhere to the cathode as pure copper. Current is a movement of electrons in the external circuit, but inside the cell the current, called electrolytic current, is a movement of positive and negative ions. The chemical reactions in the cell will continue until all the anode has passed into solution and has been deposited on the cathode.

28.4 ELECTROLYTIC CELL WITH INERT ELECTRODES

Certain materials will not combine readily with the ions in an electrolyte. Typical of these are carbon and platinum. If one of these two materials is used as the anode in a electrolytic cell there will be no chemical combining of anode material with electrolyte ions when current passes through the cell. In a copper sulphate solution the positive ions will still be attracted to the cathode and the negative ions will migrate to the anode. (Figure 28.4).

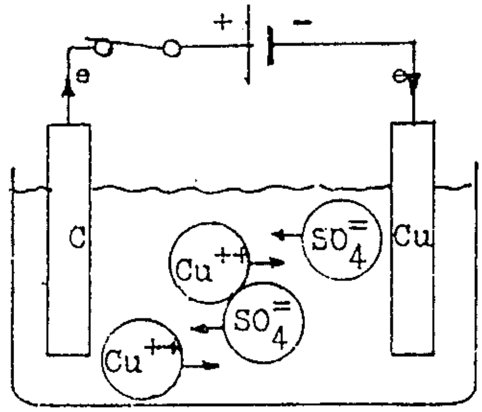

Figure 28.5

At the anode the negative sulphate ions combine with hydrogen from the water, releasing electrons and producing oxygen. The released electrons are accepted by the positive copper ions at the cathode. The chemical reactions continue until all the copper ions in the copper sulphate electrolyte have been deposited as pure copper on the cathode. The electrolyte changes from copper sulphate to sulphuric acid.

28.5 MASS OF A MATERIAL DEPOSITED ON THE CATHODE

The mass of the material from the electrolyte, that is deposited on the negative cathode is proportional to three factors. These are -

1. The electrochemical equivalent of the material (Z).
2. The current passing through the cell (I).
3. The time the continuous current passes through the cell (t).

$$m = Z \; I \; t$$

Where —

m = mass in kilograms.

Z = electrochemical equivalent in kilograms per coulomb.

I = current in ampères

t = time in seconds

The electrochemical equivalents of some of the materials used in electrolytic cells is shown in Table 28.2.

Table 28.2

ELEMENT	ELECTROCHEMICAL EQUIVALENT KILOGRAMS PER COULOMB
Chromium	0.91×10^{-7}
Copper	3.29×10^{-7}
Nickel	3.05×10^{-7}
Silver	11.2×10^{-7}
Zinc	3.37×10^{-7}

Example 28.1

Calculate the mass of a metal whose electrochemical equivalent is 3.05×10^{-7} kilograms per coulomb, that will be deposited on the cathode of an electrolytic cell when 10 amperes passes through the cell for 10 minutes.

$$Z = 3.05 \times 10^{-7} \text{ kg C}^{-1}$$
$$I = 10 \text{ A}$$
$$t = 10 \times 60 = 600 \text{ seconds}$$
$$m = ?$$

$$m = ZIT$$
$$= 3.05 \times 10^{-7} \times 10 \times 600$$
$$= 1.83 \times 10^{-3} \text{ kg}$$

Example 28.2

Determine the current required to flow in a electrolyte, whose electrochemical equivalent is 3.29×10^{-7} kg C^{-1}, if 3 gms of material is deposited on a cathode in one hour.

$$m = 3 \times 10^{-3} \text{ kg}$$
$$z = 3.29 \times 10^{-7} \text{ kg C}^{-1}$$
$$I = ?\text{ A}$$
$$t = (1 \times 60 \times 60) \text{ s}$$

$$m = Z\,I\,t$$
$$I = \frac{m}{Z t}$$
$$= \frac{3 \times 10^{-3}}{3.29 \times 10^{-7} \times 60 \times 60}$$
$$= 2.53 \text{ A}$$

Electrolytic cells are extensively used in electroplating and the refining of metals. In electroplating the part to be plated is made the cathode of the cell. Metals such as copper are refined by making the impure copper the anode of a cell and using the process discussed earlier to deposit the pure copper on the cathode. These processes are fully discussed in Chapter 6.

Equation in this chapter

(1) $M = Z\,I\,t$

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(1) One hundred amperes was maintained between two copper electrodes in a copper sulphate solution for 2 hours. Calculate the mass of the copper deposited. (Z for copper = 3.29×10^{-7} kg C^{-1}).

(2) Calculate the constant current required to deposit 100 gms of chromium in an electroplating process if the process takes 45 minutes (Z of chromium = 0.91×10^{-7} kg C^{-1}).

(3) How long would it take for 50 gms of silver to be deposited from a silver nitrate (Z = 11.2×10^{-7} kg C^{-1}) solution if a current of 75 A flows through the solution.

(4) How long would it take to silver plate an article with 1 gm of silver using 5 amperes of current (Z = 11.2×10^{-7}).

(5) Calculate the value of steady current which will deposit 100 gms of copper from a copper sulphate solution (Z = 3.29×10^{-7}) in 5 hours.